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HEATS OF COMBUSTION AND OF FORMATION OF THE NORMAL PARAFFIN HYDROCARBONS IN THE GASEOUS STATE, AND THE ENERGIES OF THEIR ATOMIC LINKAGES

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ABSTRACT

From the data recently obtained in this laboratory on the heats of combustion of methane, ethane, propane, normal butane, and normal pentane, reliable values are deduced for the heats of combustion of all the other normal paraffin hydrocarbons in the gaseous state. For normal C_nH_{2n+2} (gas), with $n>5$, the heat of combustion, at a temperature of 25 C and a constant total pressure of 1 atmosphere, in gaseous oxygen to form gaseous carbon dioxide and liquid water, is $60.40+n(157.00\pm0.08)$ $\mathrm{k-cal}_{15}$ per mole. (This unit of energy is a defined one and is derived from the fundamental international joule by means of the factor 1.00040/4.1850.)

The following generalization is made: In any organic molecule containing a normal alkyl group of more than 5 carbon atoms, the addition of a CH_2 group to the normal alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at a temperature of 25 C and a constant total pressure of 1 atmosphere, of 157.00 ± 0.08 $\mathrm{k-cal}_{15}$ per mole.

From these and other data values are computed for the heats of formation, from hydrogen and β-graphite and diamond, respectively, of all the normal paraffin hydrocarbons in the gaseous state at temperatures of 25 C and 0 Kelvin.

The energy of dissociation, at zero Kelvin, of a gaseous normal paraffin hydrocarbon, C_nH_{2n+2}, into gaseous carbon and hydrogen atoms, is shown to be a linear function of n above, but not linear below, $n=6$. The deviations from linearity for the latter are in the direction of greater stability of the molecule and have the following values: Methane, 4.81 ± 0.08; ethane, 1.59 ± 0.14; propane, 0.83 ± 0.19; normal butane, 0.46 ± 0.27; normal pentane, 0.13 ± 0.37, k-cal per mole.

It is shown that for the normal paraffin hydrocarbons, and for carbon and hydrogen atoms in the normal state, the energy evolved in the reaction C (gas) + 2H(gas) + C_nH_{2n+2} (gas) = $C_{n+1}H_{2n+4}$ (gas), for $n>5$, at 0 Kelvin, is $-\Delta H_0^0=(20.8\pm0.9)+D_{co}$ $\mathrm{k\text{-}cal}_{15}$ per mole (D_{co} is the energy of dissociation of CO at 0 Kelvin); and any assignment of values for D_{co}, for the energy of excitation of the carbon atom to the ^5S state, and for the energies of the 1 C–C and 2 C–H bonds formed in the reaction must satisfy this relation.

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I. INTRODUCTION

In this paper the writer utilizes the data on the heats of combustion of methane, ethane, propane, normal butane, and normal pentane recently obtained in this laboratory (1, 25)[1] for the following purposes: First, to predict accurate values for the heats of combustion of the normal gaseous paraffin hydrocarbons containing more than 5 carbon atoms; second, to compute values for the heats of formation of all the normal paraffin hydrocarbons in the gaseous state; and third, to test the accuracy of the postulate of the constancy of the energies of the atomic linkages in these molecules.

Because of the increasing industrial importance of vapor phase reactions involving the paraffin hydrocarbons, there is great need for values of the heats of formation of these substances in the gaseous state, for making calculations of the chemical equilibria involved.

The heats of combustion of hydrocarbons have been of considerable interest to the physical chemist for many years. Speculation concerning the influence of structure and of the number of carbon atoms upon the energy content of hydrocarbon molecules began as early as 1869, when Hermann (2) utilized for this purpose the data on heats of combustion obtained by Favre and Silbermann (4) about 15 years earlier.

From the results of his own measurements, reported in 1886 in the fourth volume of his monumental treatise on thermochemistry, Thomsen (3) showed that, in general, the addition of a CH_2 group to any molecule in the gaseous state resulted in an increase in its heat of combustion of about 158 kilocalories per mole. And, in particular, Thomsen's values for methane, ethane, propane, isobutane, and tetramethylmethane showed constant successive differences in the heats of combustion, at constant pressure and a temperature of 18 C, of 158.34 ± 0.20 kilocalories per mole.

Except for the meager data of Berthelot and Matignon (5) on ethane and propane, and the isolated value of Roth and Machlett (6) on pentane, no data on the heats of combustion of the gaseous paraffin hydrocarbons above methane were reported during the half century following Thomsen's measurements. Thus it was only natural that Thomsen's data were used to substantiate the almost universally accepted postulate of the constancy of the energies of the C–C and C–H linkages in the saturated hydrocarbon molecules.

Many calculations have been made in recent years concerning the postulate of the constancy of bond energies in the paraffin hydrocarbons. In his recent book on "The Covalent Link in Chemistry", published in 1933, Sidgwick (7) writes: " * * * and so the values of the heats of formation of the [atomic] links [in the paraffin hydrocarbons] should be independent of the number of atoms in the molecule, as in fact they are found to be."

In particular, one may cite the recent, 1932, calculations of Pauling (8) who showed that, using the values given by Kharasch[2] (9) for the heats of combustion of methane, ethane, propane, butane, hexane, and heptane, the energies of formation from gaseous atoms calculated on the assumption of constant energies for the C–H and C–C bonds were practically identical with the values computed from heats of combustion plus some auxiliary data.[3] The differences between the values calculated by the two methods were such as to be equivalent to errors of less than 0.1 percent in the heats of combustion, or about 0.2 kilocalorie per carbon atom. This agreement is quite extraordinary because it borders on the very limit of the calorimetric precision obtainable by Thomsen (3), and there must be superimposed upon his calorimetric uncertainty errors due to the large corrections for impurities in the samples of hydrocarbons burned by him. This latter uncertainty is probably much greater than Thomsen's calorimetric error because his various samples had the following empirical formulas: Ethane, $C_2H_{6.054}$, $C_2H_{6.033}$; propane, $C_3H_{7.991}$; isobutane, $C_4H_{9.748}$, $C_4H_{9.899}$; tetramethylmethane; $C_5H_{11.78}$, $C_5H_{11.64}$. Thomsen assumed that his last sample of pentane was, in mole percent, 78.5 C_5H_{12}+21.5 C_4H_8.

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[1] Figures in parentheses here and throughout the text refer to the references at the end of this paper, p. 35.

[2] The values given by Kharasch (9) for methane, ethane, propane, and butane are based on the calorimetric data of Thomsen (3).

Because of these facts, it has seemed desirable that an accurate test be made of the postulate of the constancy of the energies of the atomic linkages in the simple paraffin hydrocarbon molecules, by discovering, if possible, any real deviation from linearity in the heats of combustion of the members of the series. With the data on heats of combustion recently obtained in this laboratory (1), it is now possible to submit the postulate to a more rigorous test.

II. HEATS OF COMBUSTION

According to prevailing ideas, the heats of combustion of the paraffin hydrocarbons in the gaseous state should show constant differences between successive members of the series. That is to say, the heat of combustion will be a linear function of the number of carbon atoms,

$$Qc = A + Bn \tag{1}$$

where Qc is the heat of combustion of a gaseous normal paraffin hydrocarbon containing n carbon atoms, B is the constant increment per carbon atom or CH_2 group, and A is a constant. This relation may be expressed also as

$$(Qc - A)/n = B \tag{2}$$

The following are the data recently obtained in this laboratory (1) on the heats of combustion of the gases at a temperature of 25 C and a constant total pressure of 1 atmosphere, in k-cal$_{15}$ per mole: [4]

Methane	212. 79±0. 07
Ethane	372. 81±0. 11
Propane	530. 57±0. 12
Normal butane	687. 94±0. 15
Normal pentane	845. 27±0. 21

Examination of these values shows that the successive differences are 160.02, 157.76, 157.37, and 157.33, respectively. These differences are quite significantly not constant, but are apparently approaching a constant value with increasing number of carbon atoms. In figure 1 is plotted, against the number of carbon atoms, the function $(Qc-60.40)/n$. The value of the constant, 60.40, has been chosen so that the values of $(Qc-60.40)/n$ will approach a constant value at about $n=6$. That this relation adequately represents the data is corroborated by the values which have been included on the plot for gaseous normal heptane and gaseous normal octane.

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[3] The nature of the calculation is such that the use of different values for the subsidiary data changes only the actual values of the C–H and C–C bond energies, not their constancy from one molecule to another. The postulate of the constancy of the energies of the atomic linkages in the normal gaseous paraffin hydrocarbons may be said to be practically substantiated if the heats of combustion of all the successive members of the series show constant differences within the limits of experimental error.

[4] These values are given in k-cal$_{15}$, which is a defined unit and is taken as equivalent to 4.1850/1.00040 international kilojoules. The fundamental unit of energy in this work is the international joule based upon standards of emf and resistance maintained at this Bureau. See p. 736 of reference (25).

The values for the heats of combustion of gaseous normal heptane and gaseous normal octane are, respectively, 1159.5 ± 0.6 and 1316.3 ± 0.7, k-cal$_{15}$ per mole at a temperature of 25 C and a constant total pressure of 1 atmosphere. These values are based upon the recent accurate data obtained by Jessup (10), in the heat division of this Bureau, on the heats of combustion of the liquid hydrocarbons at a temperature of 30 C and constant volume in a bomb calorimeter. Jessup's data have been converted according to the method of Washburn (11) to give the energy of the reaction at a pressure of 1 atmosphere. After converting to a temperature of 25 C and a constant pressure of 1 atmosphere, the writer has added the heat of vaporization, using the values 8.75 and 9.85, k-cal per mole, for normal heptane and normal octane, respectively. These values of the heat of vaporization, which are uncertain by about 0.5 percent, were obtained by the present writer from a review of the existing data which will be published in a subsequent paper. Jessup's data on the heats of combustion of liquid normal heptane and liquid normal octane are accurate to about ±0.03 percent.

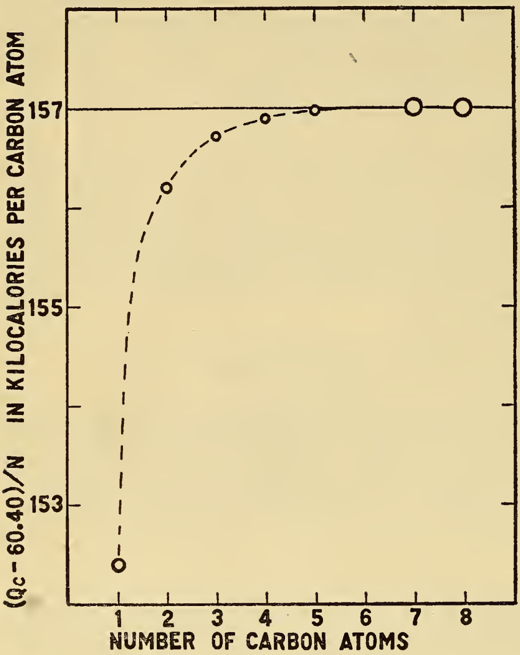

FIGURE 1.—*Relation between the heats of combustion of the normal paraffin hydrocarbons and the number of carbon atoms in the molecule.*

The scale of ordinates gives the function $(Qc-60.40)/n$, where Qc is the heat of combustion of gaseous normal C_nH_{2n+2} at a temperature of 25 C and a constant total pressure of 1 atmosphere, in k-cal$_{15}$ per mole, and n is the number of carbon atoms in the molecule. The scale of abscissae gives the number of carbon atoms in the molecule. The circles are drawn with radii representing the estimated uncertainties in the various values.

From the data displayed in figure 1, one can say that the heat of combustion of any gaseous normal paraffin hydrocarbon containing more than 5 carbon atoms is given by the following relation:

For $n>5$

$$Qc=60.40+n\ (157.00\pm0.08)\ \text{k-cal}_{15}\text{ per mole}^{5} \qquad (3)$$

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[5] See footnote to table 1.

at a constant total pressure of 1 atmosphere and a temperature of 25 C. Here Qc is the heat of the reaction

$$C_nH_{2n+2}\text{ (gas)}+\frac{3n+1}{2}O_2\text{ (gas)}=nCO_2\text{ (gas)}+(n+1)\,H_2O\text{ (liquid)} \qquad (4)$$

and n is the number of carbon atoms, which must be greater than 5. The uncertainty in the values of Qc obtained from the foregoing relation is about ±0.05 percent.

In table 1 are summarized the values for the heats of combustion of the normal paraffin hydrocarbons in the gaseous state.

Table 1.—*Summary of the values for the heats of combustion of the normal paraffin hydrocarbons in the gaseous state*

$C_{n2}H_{n+2}$ (gas)	Heat[1] of combustion at 25 centigrade and a constant total pressure of 1 atmosphere
	K-cal$_{15}$ per mole.
Methane	212.79±0.07
Ethane	372.81± .11
Propane	530.57± .12
Normal butane	687.94± .15
Normal pentane	845.27± .21
Normal hexane	1,002.40± .48
Normal heptane	1,159.40± .56
Normal octane	1,316.40± .64
Normal nonane	1,473.40± .72
Normal decane	1,630.40± .80
Normal undecane	1,787.40± .88
Normal dodecane	1,944.40± .96
Normal pentadecane	2,415.4±1.2
Normal C_nH_{2n+2} (for $n>5$)	$60.40+n\,(157.00\pm.08)$

[1] The k-cal$_{15}$ used here is a defined unit, and is derived from the fundamental international kilojoule by means of the factor 1.00040/4.1850. The values are independent of the atomic weight of carbon; 1 mole of C_nH_{2n+2} is taken as equivalent to $(n+1)$ (18.0156) grams of H_2O. The values for the first 5 members of the series are directly measured ones, the values for the others are calculated.

It will be noted that the actual heats of combustion of the first 5 members of the series differ from the values expected from the linear relation given by equation 3, by the following amounts: Methane, -4.61 ± 0.07; ethane, -1.59 ± 0.11; propane, -0.83 ± 0.12; normal butane, -0.46 ± 0.15; normal pentane, -0.13 ± 0.21, k-cal per mole, at a constant total pressure of 1 atmosphere and a temperature of 25 C.

The writer believes that it is now possible to make the following accurate generalization concerning the heats of combustion of all organic compounds containing normal alkyl groups of more than 5 carbon atoms:

In any organic molecule containing a normal alkyl group of more than 5 carbon atoms, the addition of a CH_2 group to the normal alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at a temperature of 25 C and a constant total pressure of 1 atmosphere, of 157.00 ± 0.08 k-cal$_{15}$ per mole.

III. HEATS OF FORMATION FROM THE ELEMENTS

1. AT 25 CENTIGRADE

It is conventional, in tabulating thermodynamic data concerning the free energies, heats, and entropies of formation of chemical compounds, to use as reference or standard states for the elemental substances those states in which the elements naturally exist at the standard temperature of 25 C.

Because the synthesis of the hydrocarbon molecules cannot be carried out under conditions which permit accurate calorimetric measurement, the heats of formation of these substances are computed most accurately from their heats of combustion. For this purpose it is necessary to know the heats of formation of liquid water and gaseous carbon dioxide. The standard state usually chosen for carbon is that of graphite, but this reference state is a somewhat uncertain one because Roth and his coworkers (12) have found that the heats of combustion of various graphites differ by amounts which are very much greater than the calorimetric errors. Roth found that the heats of combustion of various samples of graphite naturally grouped themselves more or less closely about two values. The samples giving the higher value had much the less spread, and Roth chose this as the more definite of the two kinds, labeling it β-graphite and the other α-graphite. Another standard state that has been proposed for carbon is that of diamond, which, though a perfectly definite state, has the apparent disadvantage that it is practically inaccessible on account of its cost. However, it may be more desirable to deal with a certain fixed reference state, even though it is practically inaccessible, than to select as standard an accessible state which is naturally variable and whose position must therefore be fixed arbitrarily. For these reasons, the present calculations on the heats of formation of the normal paraffin hydrocarbons in the gaseous state are made with reference to two standard states for carbon, β-graphite and diamond.

The heat of formation of liquid water from gaseous hydrogen and oxygen has been determined in this laboratory (1):

$$H_2\text{ (gas)} + \tfrac{1}{2}O_2\text{ (gas)} = H_2O\text{ (liquid)},\quad \Delta H^0_{298\cdot 1} = -68.313 \pm 0.010\ \text{k-cal}_{15}\ \text{per mole.} \tag{5}$$

The best values for the heat of formation of carbon dioxide can be determined from the work of Roth and his coworkers (12), who measured the heats of combustion of β-graphite and of diamond at constant volume in a bomb calorimeter. The precision of their calorimetric measurements was about ±0.03 percent, but this does not represent the uncertainty in the values deduced for the heat of formation of 1 mole of carbon dioxide, for the following reasons:

(a) The desired changes in heat content are those for the reactions

$$C(\beta\text{-graphite}) + O_2\text{ (gas)} = CO_2\text{ (gas)} \tag{6}$$

and

$$C(\text{diamond}) + O_2\text{ (gas)} = CO_2\text{ (gas)} \tag{7}$$

at a temperature of 25 C and a constant pressure of 1 atmosphere. The heat effect actually measured in the bomb is that for the process of burning a mixture of carbon with liquid paraffin in oxygen at an initial pressure of about 30 or 35 atmospheres. From this heat effect is subtracted the heat of combustion of the liquid paraffin which is determined in separate but similar experiments. As Washburn (11) has shown, the heat of combustion of carbon as determined under the conditions of the bomb process will be quite significantly different from the value of $-\Delta U$ (the decrease in internal or intrinsic energy) for reactions 6 or 7. Applying Washburn's equations to the data of Roth and Wallasch (12), who, however, do not give as complete information as is desirable for this purpose, one finds that the values of $-\Delta U$ for reactions 6 and 7 at 1 atmosphere are less than the observed heats of combustion as measured in the bomb process by about 0.10 percent, which is nearly four times the calorimetric uncertainty.

(b) The amount of reaction in the experiments of Roth and his coworkers was determined from the mass of carbon placed in the bomb. Because of the possible presence of incombustible impurities in the sample of carbon the experiment carried out in this manner may result in a low heat effect per unit mass of carbon. The uncertainty in this regard can be eliminated by determining the amount of reaction from the mass of carbon dioxide formed.

(c) Because the atomic weight of carbon[6] is uncertain to about 0.03 percent, the value deduced for the heat of combustion per mole of carbon will be uncertain to the same extent whenever the amount of reaction is determined from the mass of carbon. Determination of the amount of reaction from the mass of carbon dioxide formed reduces the uncertainty in this regard to about ±0.007 percent, if the uncertainty in the atomic weight of carbon is ±0.03 percent.

From the data of Roth and his coworkers (12) the following values are obtained for the heats of combustion of carbon at a temperature of 18 C and at constant volume in their bomb calorimeter: β-graphite, 7.856 ± 0.002 and diamond, 7.873 ± 0.005, k-cal$_{15}$ per gram, weighed in air. The densities of these samples of carbon were 2.22 and 3.50 g per cm^3, respectively, and the corresponding factors for correcting the observed weights in air to true masses are 1.0004 and 1.0002. If the atomic weight of carbon is taken as 12.007 ± 0.003, and the Washburn correction of Q to 1 atmosphere as -0.10 ± 0.03 percent, then for reactions 6 and 7 one calculates, respectively, $\Delta H^0_{298.1} = -94.20 \pm 0.08$ and -94.42 ± 0.10, k-cal$_{15}$ per mole.[7] The effect of the presence of undetected incombustible impurities in the samples of carbon used by Roth and his coworkers would be to raise these values by the amount corresponding to the weight percent of incombustible impurity. The foregoing value for the heat of formation of 1 mole of carbon dioxide from β-graphite and oxygen is to be compared with the present accepted value, 94.24, which was obtained (14) from Roth's value by converting his weights in air to true masses and using 12.00 as the atomic weight of carbon.

The existing data on the heat of formation of carbon dioxide may therefore be said to be quite unsatisfactory, and an accurate determination of this fundamental thermal constant is urgently needed. Any new determination of the heat of formation of carbon dioxide carried out by combustion of carbon in a bomb calorimeter should provide (a) for the accurate specification of the conditions of the bomb process in order that the Washburn (11) correction may be made accurately, and (b) for the accurate determination of the amount of the reaction, preferably from the mass of carbon dioxide formed, in order to make insignificant the uncertainty in the value of the atomic weight of carbon and to eliminate the effect of the possible presence of incombustible impurities in the samples of carbon.

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[6] The value for the atomic weight of carbon given in the 1934 report of the International Committee on Atomic Weights (13) is 12.00. A large body of evidence has been accumulated which indicates that this value is low by about 0.04 to 0.08 percent. Presumably the changing of the old value to a new one has been delayed until such time as the uncertainty in the new value becomes significantly less than the difference between the present value and what will be the new one.

[7] For reactions 6 and 7 at 1 atmosphere, ΔH differs from ΔU by 0.003 k-cal per mole.

Because the uncertainty in the present value for the heat of formation of carbon dioxide is relatively so large, there is no advantage to be gained in changing the present accepted value, 94.24, to the value deduced above, 94.20 ± 0.08, and, accordingly, for reaction 6, the value

$$\Delta H^0_{298.1} = -94.24 \pm 0.10 \text{ k-cal}_{15} \text{ per mole} \qquad (8)$$

is used in this paper.

The data of Roth and his coworkers yield for the transition

$$\text{C}(\beta\text{-graphite}) = \text{C(diamond)},\ \Delta H^0_{298.1} = 0.22 \pm 0.07 \text{ k-cal}_{15} \text{ per mole.} \qquad (9)$$

Hence to be consistent with equation 8 one must use for the reaction given by equation 7

$$\Delta H^0_{298.1} = -94.46 \pm 0.10 \text{ k-cal}_{15} \text{ per mole.} \qquad (10)$$

Combination of equations 5, 6, and 8 with the values for the heats of combustion of the normal paraffin hydrocarbons yields for the reaction,

$$n\text{C}(\beta\text{-graphite}) + (n+1)\text{H}_2 \text{ (gas)} = \text{C}_n\text{H}_{2n+2} \text{ (gas)}, \qquad (11)$$

$$\Delta H^0_{298.1} = Qc_{298.1} - n(162.55 \pm 0.10) - (68.313 \pm 0.010) \text{ k-cal}_{15} \text{ per mole.} \qquad (12)$$

Here $\Delta H^0_{298.1}$ is the increase in heat content for the reaction of forming the normal gaseous paraffin hydrocarbon from β-graphite and gaseous hydrogen, $Qc_{298.1}$ is the heat evolved in the combustion of the hydrocarbon gas at a temperature of 25 C and a constant total pressure of 1 atmosphere, and n is the number of carbon atoms in the hydrocarbon molecule. For $n > 5$

$$\Delta H^0_{298.1} = -(7.913 \pm 0.010) - n(5.55 \pm 0.13) \text{ k-cal}_{15} \text{ per mole.} \qquad (13)$$

With diamond as the standard state for carbon the analogous equations are:

$$n\text{C(diamond)} + (n+1)\text{H}_2 \text{ (gas)} = \text{C}_n\text{H}_{2n+2} \text{ (gas)}, \qquad (14)$$

$$\Delta H^0_{298.1} = Qc_{298.1} - n(162.77 \pm 0.10) - (68.313 \pm 0.010) \text{ k-cal}_{15} \text{ per mole;} \qquad (15)$$

and for $n > 5$,

$$\Delta H^0_{298.1} = -(7.913 \pm 0.010) - n(5.77 \pm 0.13) \text{ k-cal}_{15} \text{ per mole.} \qquad (16)$$

The values computed from these equations are given in table 2.

TABLE 2.—*The heats of formation, from the elements, of the gaseous normal paraffin hydrocarbons, at 25 centigrade and 0 Kelvin*

C_nH_{2n+2} (gas)	nC(β-graphite)+$(n+1)H_2$ (gas) $=C_nH_{2n+2}$ (gas)		nC(diamond)+$(n+1)H_2$ (gas) $=C_nH_{2n+2}$ (gas)	
	$\Delta H^0_{298.1}$ *K-cal₁₅ per mole*	ΔH^0_0 *K-cal₁₅ per mole*	$\Delta H^0_{298.1}$ *K-cal₁₅ per mole*	ΔH^0_0 *K-cal₁₅ per mole*
Methane	−18.07±0.12	−16.18±0.13	−18.29±0.12	−16.53±0.13
Ethane	−20.60± .23	−16.99± .24	−21.04± .23	−17.69± .24
Propane	−25.39± .32	−20.27± .34	−26.05± .32	−21.32± .34
Normal butane	−30.57± .43	−23.93± .46	−31.45± .43	−25.33± .46
Normal pentane	−35.79± .54	−27.64± .60	−36.89± .54	−29.39± .60
Normal hexane	−41.21± .72	−31.52± .81	−42.53± .72	−33.62± .81
Normal heptane	−46.76± .84	−35.55± .97	−48.30± .84	−38.00± .97
Normal octane	−52.31± .96	−39.58±1.12	−54.07± .96	−42.38±1.12
Normal nonane	−57.86±1.08	−43.61±1.26	−59.84±1.08	−46.76±1.26
Normal decane	−63.41±1.20	−47.64±1.40	−65.61±1.20	−51.14±1.40
Normal undecane	−68.96±1.32	−51.67±1.54	−71.38±1.32	−55.52±1.54
Normal dodecane	−74.51±1.44	−55.70±1.68	−77.15±1.44	−59.90±1.68
Normal pentadecane	−91.2 ±1.8	−67.8 ±2.1	−94.5 ±1.8	−73.0 ±2.1
Normal C_nH_{2n+2} (for $n>5$)	$-7.91-n(5.55\pm0.12)$	$-7.34-n(4.03\pm0.14)$	$-7.91-n(5.77\pm0.12)$	$-7.34-n(4.38\pm0.14)$

NOTE.—The estimated uncertainties given here represent the absolute error in each of the values. The accuracy of the difference between any two values in a given column is equal to $\pm0.12\,\Delta n$ at 25 centigrade and to $\pm0.14\Delta n$ at 0 Kelvin.

2. AT 0 KELVIN

With the recent development of methods for calculating accurate values of thermodynamic quantities from spectroscopic data, it has been especially convenient to compute, for a given substance, values of the free energy function $(F^0-E^0_0)/T$, where F^0 is the free energy of the substance at the temperature T and E^0_0 (or U^0_0) is the internal energy of the substance at the absolute zero (15). Combination of the values of this function at any given temperature for all the substances participating in a given reaction yields the value of $(\Delta F^0 - \Delta E^0_0)/T$. In order to obtain a value for the free energy of the reaction it is necessary to have values for ΔE^0_0, which in the large majority of cases must be obtained from calorimetric data on heats of reaction. For this reason there is included here a tabulation of the values of ΔE^0_0 (or ΔU^0_0), which is equal to ΔH^0_0, and is the increase in internal or intrinsic energy at the absolute zero accompanying the formation of the gaseous normal hydrocarbon from its elements, carbon and hydrogen, all in their standard states.

For this calculation there are needed the values of $H^0_{298.1}-H^0_0$ for carbon, hydrogen, and the gaseous hydrocarbons, which are, in k-cal$_{15}$ per mole: C(β-graphite), 0.251 ± 0.006; C(diamond), 0.125 ± 0.013; H_2 (gas), 2.023 ± 0.001; CH_4 (gas), 2.395 ± 0.001; C_nH_{2n+2} (gas) (for $n>1$), $1.445+n\ (0.754\pm n\%)$.

The values for carbon are taken from Rodebush's compilation in the International Critical Tables (16); that for hydrogen from Giauque (15); that for methane from Kassel (17); and those for the normal hydrocarbons above methane from unpublished calculations by Kassel (18).

For the reaction given by equation 11

$$\Delta H^0_0 = Qc_{298.1} - n(160.28\pm0.10) - (66.290\pm0.010) - (H^0_{298.1}-H^0_0)\ [C_nH_{2n+2}\ (\text{gas})]\ \text{k-cal}_{15}\ \text{per mole}, \quad (17)$$

and for $n>5$

$$\Delta H^0_0 = -(7.335\pm0.032) - n(4.03\pm0.14)\ \text{k-cal}_{15}\ \text{per mole}. \quad (18)$$

For the reaction given by equation 14

$$\Delta H^0_0 = Qc_{298.1} - n(160.63 \pm 0.10) - (66.290 \pm 0.010) - (H^0_{298.1} - H^0_0)\ [C_nH_{2n+2}\ (\text{gas})]\ \text{k-cal}_{15}\ \text{per mole,} \quad (19)$$

and for $n > 5$

$$\Delta H^0_0 = -(7.335 \pm 0.032) - n(4.38 \pm 0.14)\ \text{k-cal}_{15}\ \text{per mole} \quad (20)$$

The values calculated from these equations are given in table 2.

IV. CHANGE IN HEAT CONTENT FOR THE REACTION: nCO (gas) + (n+1) H_2 (gas) = n/2 O_2 (gas) + C_nH_{2n+2} (gas)

From data obtained in this laboratory (1), it is possible to evaluate accurately the change in heat content at a temperature of 25 C. for the reaction

$$n\text{CO (gas)} + (n+1)\ H_2\ (\text{gas}) = n/2\ O_2\ (\text{gas}) + C_nH_{2n+2}\ (\text{gas}): \quad (21)$$

$$\Delta H^0_{298.1} = Qc_{298.1} - n\ (135.936 \pm 0.032) - (68.313 \pm 0.010)\ \text{k-cal}_{15}\ \text{per mole;} \quad (22)$$

for $n > 5$

$$\Delta H^0_{298.1} = n(21.06 \pm 0.09) - (7.913 \pm 0.010)\ \text{k-cal}_{15}\ \text{per mole.} \quad (23)$$

In order to evaluate the change in heat content for reaction 21 at the absolute zero, values of $H^0_{298.1} - H^0_0$ are needed for the gaseous hydrocarbons, hydrogen, carbon monoxide, and oxygen. The data for hydrogen and the hydrocarbons are given in the preceding section; the values for carbon monoxide and oxygen, respectively 2.066 ± 0.001 and 2.068 ± 0.001 k-cal$_{15}$ per mole, are taken from the calculations of Johnston and his coworkers (19).

For the reaction given by equation 21

$$\Delta H^0_0 = Qc_{298.1} - n\ (132.880 \pm 0.032) - (66.290 \pm 0.010) - (H^0_{298.1} - H^0_0)\ [C_nH_{2n+2}\ (\text{gas})]\ \text{k-cal}_{15}\ \text{per mole;} \quad (24)$$

and for $n > 5$

$$\Delta H^0_0 = n(23.37 \pm 0.11) - (7.335 \pm 0.032)\ \text{k-cal}_{15}\ \text{per mole.} \quad (25)$$

The values computed from equations 24 and 25 are, respectively, in k-cal$_{15}$ per mole: Methane, 11.22 ± 0.08; ethane, 37.81 ± 0.14; propane, 61.93 ± 0.19; normal butane, 85.67 ± 0.27; normal pentane, 109.36 ± 0.37; normal hexane, 132.88 ± 0.57; normal heptane, 156.25 ± 0.72; normal octane, 179.62 ± 0.86; normal nonane, 202.99 ± 0.99; normal decane, 226.36 ± 1.10; normal undecane, 249.73 ± 1.21; normal dodecane, 273.10 ± 1.32.

V. ENERGIES OF THE ATOMIC LINKAGES

The energy required to dissociate a molecule into its constituent atoms is a quantity possessing considerable importance in determining the thermodynamic stability of the molecule. The amount of this energy of dissociation is a function of the number and kind of atoms and the nature of their respective linkages.

For molecules in which the atomic linkages can be characterized as covalent, Pauling (8) has shown that the energy of dissociation of the gaseous molecule into its constituent atoms can, as a first approximation, be expressed as the sum of constant terms which are assigned to represent the energies of the various atomic linkages in the molecule. That is to say,

$$(Da)^0_0 = \Sigma m_i l_i, \tag{26}$$

where $(Da)^0_0$ is the energy absorbed at the absolute zero in the reaction of dissociating the gaseous molecule, in its normal state, into its constitutent atoms, each in the normal state, and l_i is the value assigned to represent the energy of each atomic linkage of the kind i, the number of which is m_i. If the atoms at the instant of dissociation are not in their normal or ground states, then, as pointed out by Mecke (22), there must be added to equation 26 a term for correcting the atoms to their normal states. This gives

$$(Da)^0_0 + \Sigma m_a E_a = \Sigma m_i l_i, \tag{27}$$

where E_a is the energy, referred to the normal state, of the state of the atom at the instant of dissociation, and m_a is the number of atoms.

At the instant of dissociation of the molecule C_nH_{2n+2} into its constituent atoms, the hydrogen atoms are in their normal ^2S state, while the carbon atoms are in the tetravalent ^5S state, which has an energy [8] of about 35 kilocalories above that of the bivalent normal ^3P state. If E_c is the difference in energy between the ^5S and the ^3P states of the carbon atom, and a and b are the energies to be assigned respectively to the C–H and C–C bonds, then for the molecule C_nH_{2n+2}

$$(Da)^0_0 + nE_c = (2n+2)\ a + (n-1)\ b. \tag{28}$$

$(Da)^0_0$ is the energy absorbed in the reaction,

$$C_nH_{2n+2}\ (\text{gas}) = nC\ (\text{gas}) + (2n+2)\ H\ (\text{gas}), \tag{29}$$

when all the substances are in the normal state.

Since the term nE_c is linear in n, the postulate of the constancy of the bond energies in the paraffin hydrocarbons may be said to be substantiated if the value of $(Da)^0_0$ is a linear function of n.

If D_{CO}, D_{O_2}, and D_{H_2} are the values for the energy absorbed in the reaction of dissociating, at 0 Kelvin, the gaseous molecules, CO, O_2, and H_2, in their normal states, into their respective gaseous atoms each in its normal state, then for the reaction given by equation 29.

$$(Da)^0_0 = -Qc_{298.1} + n\ (132.880 \pm 0.032) + (66.290 \pm 0.010) + (H^0_{298.1} - H^0_0)\ [C_nH_{2n+2}\ (\text{gas})] - \frac{n}{2} D_{O_2} + nD_{CO} + (n+1)D_{H_2}\ \text{k-cal}_{15} \text{ per mole}; \tag{30}$$

and for $n > 5$

$$(Da)^0_0 = -n\ (23.37 \pm 0.11) + (7.335 \pm 0.032) - \frac{n}{2} D_{O_2} + nD_{CO} + (n+1)\ D_{H_2}\ \text{k-cal}_{15} \text{ per mole}. \tag{31}$$

---

[8] The difference in energy between the ^5S state and the ^3P state of the carbon atom is known only approximately. Pauling (8) uses the value 23, while Heitler and Herzberg (23) estimate 37 kilocalories per mole.

The value for the energy of dissociation of CO is at the time of this writing the subject of much controversial opinion and of some apparently contradictory facts. The values for the energies of dissociation of H_2 and O_2 into normal atoms are (20, 21):

$$H_2 \text{ (gas)} = 2 \text{ H (gas)}, \ \Delta H_0^0 = 102.9 \pm 0.7 \text{ k-cal}_{15} \text{ per mole} \qquad (32)$$

$$O_2 \text{ (gas)} = 2 \text{ O (gas)}, \ \Delta H_0^0 = 117.4 \pm 0.7 \text{ k-cal}_{15} \text{ per mole} \qquad (33)$$

Until an accurate value for the energy of dissociation of CO is available no accurate calculation can be made of the energy of dissociation of hydrocarbon molecules into gaseous normal carbon and hydrogen atoms. And, further, until an accurate value for the difference in energy between the ^5S and ^3P states of the carbon atom is available no accurate calculation can be made of the absolute values of the energies of the C–H and C–C linkages.

However, it is possible to deduce from equations 28, 30, and 31 certain relations concerning the energies of the atomic linkages in the normal paraffin hydrocarbons, because the values of the energies of dissociation of CO, O_2, and H_2, and the value of E_c, enter linearly into the evaluation of $\Sigma m_i l_i$, and their absolute values are not required in testing the constancy of the bond energies from one molecule to another.

In the first place it is readily evident that the relation expressed by equation 28 is not true for values of n less than 6, but is true for values of n greater than 5. If $(Da)_0^0$ is the actual energy absorbed by the dissociation of normal C_nH_{2n+2} (gas) into gaseous normal carbon and hydrogen atoms, and $(2n+2)\ a+(n-1)\ b-nE_c$ is the value calculated by assuming constant values for a and b, the energies of the C–H and C–C bonds, respectively, then one obtains the following values for Δ, the deviation of $(Da)_0^0$ from linearity with n:

Normal C_nH_{2n+2} (gas)	$\Delta=(Da)_0^0-[(2n+2)a+(n-1)b-nE_c]$	
	K-cal per mole	*K-cal per carbon atom*
Methane	4.81±0.08	4.81±0.08
Ethane	1.59±0.14	0.80±0.07
Propane	0.83±0.19	0.28±0.06
Normal butane	0.46±0.27	0.12±0.07
Normal pentane	0.13±0.37	0.03±0.07
Normal $C_nH_{2n+2} (n>5)$	0.00±0.11n	0.00±0.11

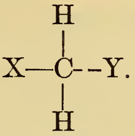
These values are plotted in figure 2.

From the above facts one can say that, within the accuracy of the present experimental data, the energy of dissociation of normal C_nH_{2n+2} (gas) into gaseous carbon and hydrogen atoms is not a linear function of n below, but is a linear function of n above, $n=6$.

If the energies of all the C—H and all the C—C linkages are assumed to be respectively equivalent throughout a given molecule then one must conclude that, below $n=6$, the strength of one or the other or both linkages increases with decreasing n.

But a better explanation may be in the distinction between various kinds of C—H and of C—C bonds in the normal paraffin hydrocarbon.

For example, one can distinguish three kinds of C—H linkages, a_0, a_1, and a_2, in the normal paraffin molecule



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ X & — & C & — & Y. \\ & & | & & \\ & & H & & \end{array}$$

a_0 is the C—H bond when $X=Y=H$,
a_1 is the C—H bond when [9] $X=H$ and $Y=R$, and
a_2 is the C—H bond when $X=Y=R$.

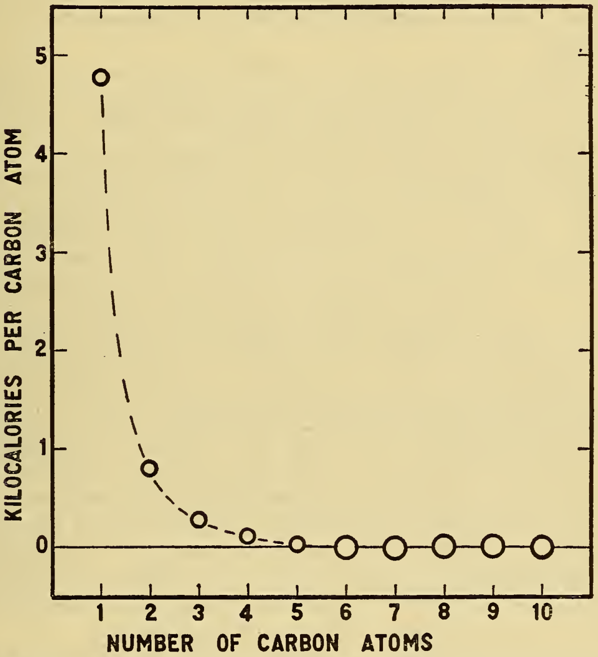
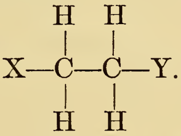


FIGURE 2.—*Deviations from linearity with the number of carbon atoms of the energy of dissociation of the normal paraffin hydrocarbon molecule into atoms.*

The scale of ordinates gives Δ, the deviation from linearity in the relation between n and the energy of dissociation, at the absolute zero, of normal C_nH_{2n+2} into gaseous carbon and hydrogen atoms, in k-cal per carbon atom. The scale of abscissae gives the number of carbon atoms in the molecule.

Similarly one can distinguish three kinds of C–C bonds, b_0, b_1, and b_2, in the normal paraffin molecule



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ X & — & C & — & C & — & Y. \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

b_0 is the C–C bond when $X=Y=H$,
b_1 is the C–C bond when $X=H$ and $Y=R$, and
b_2 is the C–C bond when $X=Y=R$.

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[9] R represents a normal alkyl radical.

On this basis the energies of the atomic linkages in the various molecules can be represented as follows:

Methane	$4a_0$.
Ethane	$6a_1+b_0$.
Propane	$6a_1+2a_2+2b_1$.
Normal butane	$6a_1+4a_2+2b_1+b_2$.
Normal pentane	$6a_1+6a_2+2b_1+2b_2$.
Normal C_nH_{2n+2}, for $n>2$	$6a_1+2(n-2)a_2+2b_1+(n-3)b_2$.

And the difference between successive members becomes constant and equal to $2a_2+b_2$ when n is greater than 3. This approximates what the experimental data indicate. In a more exact sense, however, one would need to take cognizance of the kind of atoms which are attached to the carbon atoms once removed from the bond, that is, to distinguish between various normal alkyl radicals represented by R in the above notation.

Differentiation of the various C–H linkages is not new. From measurements of the infrared absorption spectra of liquid paraffin hydrocarbons, Brackett (24) deduced that the binding force of a "primary" C–H linkage (a_1 above) is greater than that of a "secondary" C–H linkage (a_2 above) by about 3.2 percent and greater than that of a "tertiary" C–H linkage (a_3 in the above notation) by about 5.6 percent. By means of calculations involving potential energies, Eyring (26) has computed that a C–H bond in methane becomes progressively weaker as the other hydrogen atoms are replaced by methyl groups. In our notation, Eyring found that the successive differences between a_0, a_1, a_2, and a_3 were about 3.1 kilocalories.

If the bonds at the ends of the normal paraffin molecule are considered, as indicated above, to be different from the other bonds, then the addition of 1 carbon atom and 2 hydrogen atoms to C_nH_{2n+2} corresponds to the creation, at or near the middle of the molecule, of 1 C–C bond and 2 C–H bonds. And since the experimental data indicate that the energy of this process is constant for values of n greater than 5, one can conclude that, within the accuracy of the data, there is no interaction, with regard to energy between C, H groups that are separated by 2 or more carbon atoms. In other words, the methyl group at the end of the chain of carbon atoms has a sphere of influence that includes the C, H group twice removed from it.

For the reaction of adding 1 carbon and 2 hydrogen atoms to any normal paraffin hydrocarbon above pentane to form the next higher normal paraffin hydrocarbon one finds from equation 31 that, when $n>5$, for the reaction,

$$\text{C (gas)}+2\text{H (gas)}+C_nH_{2n+2}\text{ (gas)}=C_{n+1}H_{2n+4}\text{ (gas)}, \tag{34}$$

the energy evolved at 0 degree K is

$$-\Delta H_0^0=(-23.37\pm0.11)-1/2\ D_{O_2}+D_{CO}+D_{H_2}\text{ k-cal}_{15}\text{ per mole.} \tag{35}$$

Substituting the values for D_{O_2} and D_{H_2} from equations 32 and 33 gives

$$-\Delta H_0^0=(20.8\pm0.9)+D_{CO}\text{ k-cal}_{15}\text{ per mole.} \tag{36}$$

When corrected for the energy of excitation of the carbon atom from the normal ^3P state to the ^5S state, the values given by equations 35 and 36 may be said to represent the energy associated with 1 C–C and 2 C–H linkages at or near the middle of any gaseous normal paraffin hydrocarbon molecule above pentane. Then using the notation already defined.

$$2a_2+b_2=(20.8\pm 0.9)+D_{co}+E_c \text{ k-cal}_{15} \text{ per mole.} \tag{37}$$

And any assignment of values for D_{co}, for the energy of excitation of the carbon atom to the ^5S state, and for a_2 and b_2, the energies of the C–C and C–H bonds formed in reaction given by equation 34, must satisfy the relation expressed by equation 37. In general, any assignment of values must satisfy the relation

$$\Sigma m_i l_i=(110.2\pm 0.7)+n(20.8\pm 0.9)+n(D_{co}+E_c)+\Delta \text{ k-cal}_{15} \text{ per mole.} \tag{38}$$

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